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The Fluidity Method for the Determination of Association. II[a]

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This part contains fluidity data for about 346 liquids to be used for reference. They are arranged as fluidities at particular temperatures. Temperatures at particular fluidities were also obtained and from the latter tables, associations were calculated. The factors affecting association are briefly discussed which leads us to a tentative classification of associating and protecting groups. Finally the distinction between association, polymerization and condensation and polymerization is discussed.

THE authors have brought together the available data on the fluidities of pure substances, elementary and compound at 0°, 10°, 20°, 30°, 40°, 60°, 80°, 100°, Table XXV. The absolute temperatures corresponding to the fluidities of 10, 50, 100, 200, 300, 400 and 500 rhes have been obtained graphically and from these, corresponding associations have been calculated. The association varies but slightly with the fluidity, hence, only the range of values of the association n is given in the table. To save space the complete tables of temperatures and associations are omitted.

Association of Compounds

Introduction

To obtain the true temperature (absolute) required to produce a certain fluidity in a compound, the calculated temperature given in Tables XXII to XXV must be multiplied by the association factor of the compound. The results of the work of Bingham, Darrall and Fornwalt[b] prove that association depends to a high degree upon the constitution and in a manner which is readily understandable. In the first place, there are certain associating groups which accentuate the association, notably NH_2, OH, COOH, CO, and SH. On the other hand, alkyl residues are very little associated and therefore they tend to lower the association of the molecules in which they occur depending upon the magnitude and the constitution of this alkyl residue. The more exposed an associating group is, the higher will be the association; and the more fully it is surrounded by alkyl groups, the lower will be the association. A recent accumulation of fluidity data from the literature[c] has made possible a more exhaustive study of the various effects of composition and constitution on association; and several new observations have been made.

Enumeration and discussion of effects on association

1. The addition of each methylene group lowers the association approximately nine percent. Using the new atomic temperature values (of Tables XXII to XXV), we have recalculated

[a] Part I appeared in J. Rheology 3, 221 (1932).

[b] Bingham, Darrall and Fornwalt, J. Rheology 1, 174, 372 (1930).

[c] J. Rheology 2, 10 (1931); I. C. T.

TABLE XXV. *Fluidity data of organic compounds in rhes at regular intervals of temperature.**

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	n
1.	CCl_4	Carbon tetrachloride (70)	73.9	87.9	102.9	118.5	135.1	171.0					(1.09) – (1.00)
2.	CS_2	Carbon disulfide (70)	232.1	252.2	271.7	292.6	313.1						(0.93) – (1.02)
3.	$CHBr_3$	Bromoform (2) (22)	37.6	45.1	48.5	60.2	68.2	85.0	102.2				(1.01) – 1.01
4.	$CHCl_3$	Chloroform (70)	142.6	159.3	176.6	195.1	214.4	255.4					(1.02) – (1.06)
5.	CHN	Hydrogen cyanide (30)	412.	452.	497.								
6.	CH_2Br_2	Methylene bromide (24)			*81.6*$_{25}$°								(1.16) (1.16)
7.	CH_2Cl_2	Methylene chloride (70)	186.0	207.3	229.1	251.6	274.8						(1.15) – (1.19)
8.	CH_2O_2	Formic acid (70)		44.4	55.9	68.6	81.9	112.2	146.1	184.2			(2.02) – (2.28)
9.	CH_3I	Methyl iodide (70)	167.8	186.0	204.7	224.1	244.0						(0.98) – (1.05)
10.	CH_3NO	Formamide (22) (52) (25)	13.2	19.2	25.8	33.4	42.0	62.5	87.0	(119.0)	(153.0)		(2.00) – (3.40)
11.	CH_3NO_2	Nitromethane (20) (57)	118.6	134.3	151.8	170.0	190.1	232.8	279.0				(2.18) – (2.69)
12.	CH_4O	Methyl alcohol (70)	123.6	145.4	168.9	193.6	221.1	285.1					(1.93) – (1.89)
13.	$C_2Cl_3F_3$	1,1,2-Trichloro-1,2,2-trifluoroethane (68.5)			143.3	162.8	183.0						(1.00) – 1.00
14.	C_2Cl_4	Tetrachloroethylene (70)	87.6	99.5	111.6	124.2	137.4	164.6	194.2	226.3	260.5		(0.92) – (1.01)
15.	C_2HBr_3O	Bromal (27)			17.0	21.4	26.8	40.0	57.2	79.1			(1.05) – 1.02
16.	C_2HCl_3	Trichloroethylene (34)				190.	207.	242.	279.				0.99 – (1.02)
17.	C_2HCl_3O	Chloral (27)			72.5	85.4	99.0	130.	167.8				(1.17) – (1.13)
18.	C_2HCl_5	Penta chloroethane (34) (63)	26.8	33.2	40.0	48.8	57.6	77.8	100.0				(1.02) – 1.05
19.	$C_2HF_3O_2$	Trifluoroacetic acid (68.5)			114.6	133.1	153.3	198.2					(1.62) – 1.71
20.	$C_2H_2Br_2$	1,2-Acetylene dibromide (70)	81.0	92.3	103.8	115.8	128.0	153.7	181.3	210.6			(1.00) – (1.00)
21.	$C_2H_2Cl_2F_2$	1,1-Dichloro-2,2-difluoroethane (68.5)			140.2	159.7	180.5	213.7					1.20
22.	$C_2H_2Cl_3F$	1,1,2-Trichloro-2-difluoroethane (68.5)			93.5	107.0	122.0	153.7					1.14
23.	$C_2H_2Cl_4$	1,1,2,2,-Tetrachloroethane (19) (34) (22)	37.66	46.58	56.0	66.5	76.8	101.4	131.1				(1.13) – (1.08)
24.	$C_2H_2F_2O_2$	Difluoroacetic acid (68.5)			33.5	42.8	52.5	77.2					(2.02)
25.	$C_2H_3BrF_2$	1-Bromo-2,2-difluoroethane (68.5)			127.4	143.	161.1						1.24
26.	$C_2H_3Br_3O_2$	Bromal hydrate (27)					2.17	9.17	23.8	50.0			1.23 – 1.13
27.	C_2H_3NS	Methyl thiocyanate (5)	95.19	110.4	126.3	142.4	160.3	196.6	236.1	275.6			1.65 – (1.83)
28.	$C_2H_4Br_2$	Ethylene bromide (70)	40.9	48.9	57.7	67.8	77.9	99.8	123.3	149.3	177.3		(1.18) – (1.09)
29.	$C_2H_4Cl_2$	1,1-Dichloroethane (70)	160.1	182.1	203.5	226.7	250.5						(1.12) – (1.11)
30.	$C_2H_4Cl_2$	Ethylene chloride (70)	88.6	103.7	119.7	136.8	154.5	192.1	234.2				(1.31) – (1.25)
31.	$C_2H_4N_2O_6$	Ethylene glycol dinitrate (56)		17.5	23.8	30.4	38.5	54.9					
32.	$C_2H_4F_2O$	2,2-Difluoroethyl alcohol (68.5)			37.73	49.25	63.27	96.00					(2.10)
33.	C_2H_4O	Acetaldehyde (70)	373.4	409.5	450.1								(1.27) – (1.28)
34.	C_2H_4O	Ethylene oxide (49)	312.3	343.0	*173.0*$_{-50}$°	*200.0*$_{-40}$°		*228.0*$_{-30}$°		*256.4*$_{-20}$°		*285.0*$_{-10}$°	1.33 – 1.36
35.	$C_2H_4O_2$	Acetic acid (70)			82.0	96.2	110.7	142.3	178.0	217.8			(1.71) – (1.95)
36.	$C_2H_4O_2$	Methyl formate (70)	232.3	259.3	287.0	314.9							(1.39) – (1.45)
37.	C_2H_5Br	Ethyl bromide (70)	208.6	231.1	254.3	278.3							(1.01) – (1.01)
38.	C_2H_5FO	2-Fluoroethyl alcohol (68.5)			52.92	64.94	80.20	113.6					(2.10)
39.	C_2H_5I	Ethyl iodide (70)	138.5	154.6	171.0	188.3	206.1	243.5					(0.99) – (1.04)
40.	C_2H_5NO	Acetamide (25)									70.0	94.3	(2.84) – 3.20
41.	$C_3H_5NO_2$	Methyl carbamate (65)						50.0	82.2	119.5			2.40 – 2.64
42.	C_2H_6O	Ethyl alcohol (70)	56.3	68.8	83.5	100.7	120.3	168.9					1.98 – (1.90)
43.	$C_2H_6O_2$	Ethylene glycol (6)			5.022	7.602	10.95	20.22	33.15	50.30	71.60	96.29	2.35 – 2.54
44.	C_2H_6S	Methyl sulfide (70)	281.9	310.2	340.0	371.0							(1.06) – (1.08)
45.	C_2H_6S	Ethyl mercaptan (6)	275.2	303.2	333.5	*347.7*$_{+25}$°							(1.05) – (1.10)
46.	$C_3H_3F_3O$	1,1,1-Trifluoroacetone (68.5)		285.9									(1.244)
47.	C_3H_5Br	3-Bromopropylene (Allyl) (70)	161.0	180.7	201.1	221.9	243.6	290.2					(1.08) – (1.02)
48.	C_3H_5Cl	3-Chloropropylene (Allyl) (70)	245.6	273.7	302 7	333.6	364.8						(1.11) – (1.10)
49.	$C_3H_5F_3O$	1,1,1-Trifluoroisopropyl alcohol (68.5)			32.9	47.5	66.4						(1.82)
50.	C_3H_5I	3-Iodopropylene (Allyl) (70)	107.4	122.0	137.4	153.0	169.5	204.1	242.0	282.8			(1.00) – (1.02)

* The numbers in parentheses refer to authorities given in list of references. The association range is indicated under n.

The numbers in parentheses refer to authorities given in list of references. The association range is indicated under *n*.

TABLE XXV. (*Continued.*)

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	*n*
51.	C_3H_5N	Propionitrile (71)	184.8	207.0	230.0								(1.96)
52.	C_3H_5NS	Ethyl thiocyanate (71)	90.5	105.0	120.0								1.51
53.	$C_3H_5N_3O_9$	Glycerol trinitrate (56)		1.45	2.78	4.76	7.35	14.7					
54.	$C_3H_6Br_2$	1,2-Dibromopropane (70)	43.6	52.1	61.5	71.6	82.0	104.6	129.6	157.0	186.4	218.5	(1.11) – (0.99)
55.	$C_3H_6Br_2$	1,3-Dibromopropane (24)			*55.7*$_{25°}$								(1.14) (1.10)
56.	$C_3H_6N_2O_6$	Propylene glycol dinitrate (56)		18.0	24.6	31.9	40.7	58.5					
57.	$C_3H_6N_2O_6$	Trimethylene glycol dinitrate (56)		11.8	16.8	22.9	29.1	42.9					
58.	C_3H_6O	Allyl alcohol (70)	46.3	58.5	73.2	90.5	109.5	155.2	212.4				(1.84) – (1.65)
59.	C_3H_6O	Propionaldehyde (71)	214.1	244.3	274.6								1.37 1.36
60.	C_3H_6O	Acetone (70)	252.7	280.0	309.2	340.5	372.0						(1.28) – 1.31
61.	$C_3H_6O_2$	Propionic acid (70)	65.7	77.6	90.6	104.4	118.5	149.3	183.1	220.6	262.8	310.6	(1.52) – (1.74)
62.	$C_3H_6O_2$	Ethyl formate (70)	197.6	222.3	248.1	275.7	304.0						(1.25) – (1.35)
63.	$C_3H_6O_2$	Methyl acetate (70)	208.6	234.4	261.6	290.1	319.6						(1.23) – (1.33)
64.	C_3H_7Br	*n*-Propyl bromide (70)	154.5	173.4	192.5	213.2	234.4	280.5					(1.09) – (1.03)
65.	C_3H_7Br	Isopropyl bromide (70)	164.9	185.3	207.0	229.5	253.1						(1.06) – (1.00)
66.	C_3H_7Cl	*n*-Propyl chloride (70)	228.9	255.7	283.2	312.6	342.8						(1.13) – (1.12)
67.	C_3H_7Cl	Isopropyl chloride (70)	248.2	278.2	309.6	342.5							(1.11) – (1.09)
68.	C_3H_7I	*n*-Propyl iodide (70)	106.0	120.4	135.0	150.5	166.5	200.4	237.7	278.1			(1.00) – (1.03)
69.	C_3H_7I	Isopropyl iodide (70)	113.5	128.5	144.4	161.3	178.5	196.5	215.7	256.4			(0.98) – (1.00)
70.	C_3H_7NO	Propionamide (25)									72.5	97.1	2.79
71.	$C_3H_7NO_2$	Urethane (68) (25)						42.5	68.7	100.0	139.9		2.20 2.40
72.	C_3H_8O	*n*-Propyl alcohol (70)	25.7	34.1	44.3	56.1	71.2	108.5	159.0				(1.92) – (1.78)
73.	C_3H_8O	Isopropyl alcohol (70)	21.8	30.7	42.0	56.6	75.1	124.2	190.8				(2.01) – (1.72)
74.	C_3H_8S	*n*-Propyl mercaptan (6)	198.8	222.4	247.4	273.1							(1.07) – (1.12)
75.	C_3H_8S	Propane thiol-2 (6)	209.5	237.1	265.4	294.8	325.8						(1.04) – (1.07)
76.	C_3H_9N	Trimethyl amine (28)	*311.7*$_{-35.5°}$										(1.49)
77.	$C_3H_9O_4P$	Trimethyl orthophosphate (29.05)			44.29	54.88	65.66						
78.	C_4H_4S	Thiophene (70)	114.6	132.6	151.3	171.3	191.6	235.2	284.8				(1.14) – (1.17)
79.	$C_4H_5F_3O_2$	Ethyl trifluoroacetate (68.5)			230.2	259.9	290.0	353.8					(1.18)
80.	C_4H_5NS	Allyl thiocyanate (48) (46)			141.	155.	170.	201.	234.	(317.)	(368.)		(1.30) – (1.42)
81.	$C_4H_6F_2O_2$	1,1-Bifluoroethyl acetate (68.5)			88.34	104.9	123.3	162.7					1.49
82.	$C_4H_6F_2O_2$	Ethyl Difluoroacetate (68.5)			131.3	151.2	172.3	217.5					1.38
83.	$C_4H_6O_3$	Acetic anhydride (70)	80.2	95.2	110.6	126.9	143.8	180.2	220.1	264.5	311.2		(1.30) – (1.46)
84.	$C_4H_7FO_2$	1-Fluoroethyl acetate (68.5)			92.08	107.8	125.6	161.8					1.51
85.	$C_4H_7FO_2$	Ethyl fluoroacetate (68.5)			104.4	122.5	141.9	180.8					1.47
86.	$C_4H_7F_3O$	1,1,1-Trifluoro-*tert.*-butyl alcohol (68.5)				36.95	54.17						(1.69)
87.	$C_4H_8Br_2$	1,2-Dibromo-2-methyl propane (70)	30.0	37.7	46.0	54.8	64.5	85.6	109.6	136.2	165.5	198.2	(1.11) – (0.98)
88.	$C_4H_8N_2O_7$	Diethylene glycol dinitrate (56)		8.4	12.4	17.5	22.9	36.4					
89.	C_4H_8O	Methyl ethyl ketone (70)	185.2	209.9	235.4	262.7	291.0	350.5	416.3				(1.26) – (1.28)
90.	$C_4H_8O_2$	*n*-Butyric acid (70)	43.5	53.8	64.8	76.8	89.2	116.8	148.3	182.9	221.9	266.8	160°C./315.8
													(1.53) – (1.64)
91.	$C_4H_8O_2$	Isobutyric acid (70)	52.6	63.7	75.8	88.5	101.9	131.3	164.0	202.3	243.2	289.3	(1.49) – (1.61)
92.	$C_4H_8O_2$	Ethyl acetate (70)	172.5	196.6	222.0	249.2	276.8	336.5					(1.20) – (1.25)
93.	$C_4H_8O_2$	Methyl propionate (70)	171.5	194.6	219.2	244.5	271.3	328.1					(1.20) – (1.27)
94.	$C_4H_8O_2$	*n*-Propyl formate (70)	149.5	170.5	193.1	217.1	242.3	296.5	355.9				(1.21) – (1.30)
95.	C_4H_9Br	Isobutyl bromide (70)	121.1	138.5	156.2	175.2	194.8	237.8	286.1				(1.13) – (0.99)
96.	C_4H_9Cl	Isobutyl chloride (70)	170.7	194.1	218.5	244.6	271.9	330.7					(1.13) – (1.11)
97.	C_4H_9I	Isobutyl iodide (70)	85.8	100.0	114.5	129.4	144.4	177.0	212.7	251.7	294.0		(1.02) – (1.00)
98.	C_4H_{10}	Butane (43)	483.	528.	575.	628.	*393.*$_{-20°}$						(0.99) – (0.98)
99.	$C_4H_{10}O$	*n*-Butyl alcohol (70)	19.0	25.8	33.9	44.4	56.3	87.8	131.0	186.7			(1.85) – (1.65)
100.	$C_4H_{10}O$	Isobutyl alcohol (70)	12.6	17.9	25.6	35.0	47.2	80.3	128.2	191.6			1.95 – (1.63)

TABLE XXV. (*Continued.*)

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	n
101.	$C_4H_{10}O$	tert.-Butyl alcohol (70)				29.5	47.3	96.7	166.3				(2.10) −(1.57)
102.	$C_4H_{10}O$	Ethyl ether (70)	349.8	386.0	425.2	465.9							1.02 − 1.06
103.	$C_4H_{10}O$	Methyl propyl ether (70)	324.5	359.9	396.1	435.7							(1.06) −(1.09)
104.	$C_4H_{10}S$	Ethyl sulfide (70)	178.4	200.9	224.6	249.7	274.9	328.4	387.9				(1.02) −(1.05)
105.	$C_4H_{10}S$	*n*-Butyl mercaptan (6)	154.5	174.8	200.3	222.7	245.8	295.0	348.9				(1.07) −(1.09)
106.	$C_5H_4O_2$	Furfural (8)	41.13	50.92	61.83	73.69	86.21	111.4	142.4	173.6			1.45 − 1.51
107.	C_5H_5N	Pyridine (16) (61) (25) (32)	75.3	89.9	105.8	121.4	139.5	172.4	204.5	242.0			(1.63) −(1.89)
108.	$C_5H_7F_3O_2$	1,1,1-Trifluoroisopropyl acetate (68.5)			138.1	160.4	184.1	235.0					1.23
109.	C_5H_8	Isoprene (70)	383.7	422.0	462.9	504.9							(0.98) − 0.98
110.	C_5H_9N	*n*-Valeronitrile (3.5)	98.43	115.4	132.8	151.6	171.3	213.0	258.2	308.1			1.67 −(1.80)
111.	C_5H_{10}	Cyclopentane (18)	174.8	197.5	220.0	246.0							(1.26) −(1.27)
112.	C_5H_{10}	2-Methyl-2-butene (70)	393.4	431.6	471.5	515.2							(0.97) − 0.97
113.	$C_5H_{10}Br_2$	1,5-Dibromopentane (24)				*82.8*$_{26}$°							(1.12) −(1.10)
114.	$C_5H_{10}O$	Diethyl ketone (70)	167.6	189.9	213.7	237.7	262.8	316.6	375.9	441.2			(1.18) −(1.21)
115.	$C_5H_{10}O$	Methyl propyl ketone (70)	154.7	176.5	199.0	222.4	246.9	299.0	355.9	419.1			(1.21) −(1.24)
116.	$C_5H_{10}O_2$	*n*-Valeric acid (23) (26) (31)			44.0	53.1	63.8	88.3	116.3				1.55 − 1.57
117.	$C_5H_{10}O_2$	*n*-Butyl formate (5)	106.4	125.2	145.0	166.4	188.2	236.8	288.8	347.0			1.24 −(1.26)
118.	$C_5H_{10}O_2$	Ethyl propionate (70)	144.1	164.9	187.4	211.4	236.1	289.3	348.9				(1.13) −(1.20)
119.	$C_5H_{10}O_2$	Methyl *n*-butyrate (70)	131.4	151.8	173.5	196.3	220.4	271.3	327.7	390.8			(1.16) −(1.21)
120.	$C_5H_{10}O_2$	Methyl isobutyrate (70)	148.4	170.1	192.7	216.2	241.4	295.3	355.8				(1.15) −(1.19)
121.	$C_5H_{10}O_2$	*n*-Propyl acetate (70)	129.3	149.7	171.5	195.1	219.3	271.3	328.7	393.8			(1.16) −(1.21)
122.	$C_5H_{10}O_3$	Ethyl lactate (6)	18.80	27.17	37.30	48.97	62.17	92.64	128.3	178.7			(1.49) − 1.43
123.	$C_5H_{11}F$	*n*-Amyl fluoride (68.5)			268.5	298.2	329.0	396.2					(1.17)
124.	C_5H_{12}	*n*-Pentane (70)	352.3	390.0	429.5	470.7							(1.00) − 1.00
125.	C_5H_{12}	Isopentane (70)	365.9	405.0	447.4	489.0							(1.00) − 0.99
126.	$C_5H_{12}O$	*d*-Amyl alcohol (active) (70)	9.0	13.5	19.7	27.8	38.5	67.1	109.7	164.8	232.2		1.88 −(1.52)
127.	$C_5H_{12}O$	Isoamyl alcohol (inactive) (70)	11.6	16.5	23.2	31.2	41.6	68.9	108.1	159.2	220.0		1.83 −(1.54)
128.	$C_5H_{12}O$	tert.-Amyl alcohol (70)	7.0	13.5	21.6	33.5	48.7	92.4	151.5	229.3			1.89 −(1.44)
129.	$C_5H_{12}O$	Ethyl propyl ether (70)	251.3	281.7	314.0	348.0	383.5						(1.07) −(1.07)
130.	$C_5H_{12}O$	Methyl isobutyl ether (70)	261.0	293.1	325.6	360.3	395.6						(1.04) −(1.06)
131.	$C_5H_{12}S$	*n*-Amyl mercaptan (6)	118.1	136.0	154.7	174.0	194.4	237.4	284.1	333.9			(1.06) −(1.08)
132.	$C_5H_{12}S$	Pentane thiol-2 (6)	142.7	162.4	183.7	204.5	226.0	275.6	328.6	385.0			(1.01) −(1.03)
133.	$C_5H_{13}N$	*n*-Amyl amine (3.5)	102.0	123.7	147.1	171.5	197.3	252.3	312.1	378.2			1.66 −(1.70)
134.	$C_5H_{13}N$	Ethyl *n*-propyl amine (69)				*110.7*$_{16}$°							(1.78)
135.	$C_6H_4FNO_2$	*o*-Fluoronitrobenzene (68.5)				45.66	54.54	74.29					(1.51) −(1.65)
136.	$C_6H_4FNO_2$	*m*-Fluoronitrobenzene (68.5)				50.3	60.6	81.9					(1.48) −(1.63)
137.	$C_6H_4FNO_2$	*p*-Fluoronitrobenzene (68.5)				44.8	54.3	74.6					(1.52) −(1.65)
138.	$C_6H_4F_2$	*m*-Difluorobenzene (68.5)			174.2	195.2	216.9	264.1					1.09
139.	$C_6H_4F_2$	*p*-Difluorobenzene (68.5)	156.3	176.	197.	241.5							1.13
140.	C_6H_5Br	Bromobenzene (53)	62.5	74.8	87.1	100.2	114.0	142.4	172.4	204.0	239.	278.	(1.19) −(1.05)
141.	C_6H_5Cl	Chlorobenzene (53)	94.9	109.5	125.0	141.8	158.4	195.0	234.0	278.7	327.		(1.10) −(1.12)
142.	C_6H_5ClO	*o*-Chlorophenol (16)	9.3	15.6	23.8	32.5	43.1	66.2	92.0	118.0	144.8	172.2	(1.50) − 1.39
143.	C_6H_5ClO	*m*-Chlorophenol (69)			6.0	11.3	18.0	33.1					(1.64) −(1.55)
144.	C_6H_5ClO	*p*-Chlorophenol (69)					13.0	27.8					(1.68) −(1.57)
145.	C_6H_5F	Fluorobenzene (53) (68.5)		155.	174.	196.	218.0	268.0	325.				(1.18) −(1.22)
146.	$C_6H_5F_2N$	2,5-Difluoroaniline (68.5)			43.06	53.33	63.90	88.2					(1.80)
147.	C_6H_5I	Iodobenzene (53)	41.5	50.0	59.0	69.1	79.4	101.9	125.8	151.0	179.	209.	160°C/241.
													(1.04) −(1.05)
148.	$C_6H_5NO_2$	Nitrobenzene (13)	32.0	39.9	49.7	59.5	69.5	91.4	115.2	142.0			(1.23) −(1.77)
149.	$C_6H_5NO_3$	*o*-Nitrophenol (16) (69)					36.4	55.0	74.1				1.57
150.	C_6H_6	Benzene (70)	110.5	131.1	153.6	177.5	202.5	255.3					(1.32) −(1.22)

TABLE XXV. (*Continued.*)

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	n
151.	C_6H_6BrN	*o*-Bromoaniline (6.5)					31.38	46.35	64.81	84.14			1.46 −(1.50)
152.	C_6H_6BrN	*m*-Bromoaniline (6.5)			14.69	20.39	27.06	41.94	58.98	76.45			1.48 −(1.54)
153.	C_6H_6BrN	*p*-Bromoaniline (6.5)							55.11	72.37			1.50 −(1.56)
154.	C_6H_6FN	*o*-Fluoroaniline (68.5)			38.8	47.8	58.82	83.5					(1.73) −(1.86)
155.	C_6H_6FN	*m*-Fluoroaniline (68.5)				45.45	56.18	80.00					(1.74) −(1.87)
156.	C_6H_6FN	*p*-Fluoroaniline (68.5)			33.04	42.15	51.8	74.60					(1.77) −(1.89)
157.	C_6H_6O	Phenol (64) (14)			8.4	14.0	20.8	39.0	62.7	91.5			1.89 −(1.71)
158.	C_6H_7N	Aniline (29) (13)	9.80	15.4	22.6	31.1	41.1	64.4	91.4	121.0	153.0		(1.62) −(2.03)
159.	C_6H_{10}	Diisopropenyl (Diallyl) (70)	294.1	328.5	363.9	400.3	438.9						(0.98) −(0.97)
160.	$C_6H_{10}O$	Cyclohexanone (33)			45.7	55.0	65.2	90.3					1.53 − 1.53
161.	$C_6H_{10}O_3$	Propionic anhydride (70)	62.1	75.4	89.5	104.3	120.0	154.1	191.8	232.4	277.4	325.8	160°C/378.7
													(1.20) − 1.28
162.	C_6H_{12}	Cyclohexane (18) (21)			104.2								1.40
163.	C_6H_{12}	Methyl cyclopentane (18)	150.4	171.8	195.0	219.3							(1.19) − 1.19
164.	$C_6H_{12}O$	Cyclohexanol (33)					5.0	13.6	29.0	53.5			2.08 − 1.90
165.	$C_6H_{12}O_2$	Caproic acid (1)			31.0	38.9	47.2	66.7	89.6	115.			1.51 − 1.53
166.	$C_6H_{12}O_2$	*n*-Butyl acetate (5)	99.65	117.5	136.6	156.9	177.8	223.4	273.5	328.5			1.16 − 1.19
167.	$C_6H_{12}O_2$	Isobutyl acetate (36) (31)			139.	159.	182.	229.	282.	345.			(1.16) −(1.18)
168.	$C_6H_{12}O_2$	Ethyl *n*-butyrate (31) (51) (47)			149.8	169.1	191.	238.	289.				(1.13) −(1.17)
169.	$C_6H_{12}O_2$	Methyl *n*-valerate (31)			140.5								(1.14) −(1.19)
170.	$C_6H_{12}O_2$	*n*-Propyl propionate (31) (51)			148.								(1.13) −(1.17)
171.	$C_6H_{12}O_3$	Paraldehyde (54)		68.3	85.5								(1.22) −(1.21)
172.	C_6H_{14}	Diisopropyl (18)	202.	230.	260.	292.							1.10 − 1.09
173.	C_6H_{14}	*n*-Hexane (70) (15)	251.5	281.0	311.5	343.8	377.7	451.3					(1.03) −(1.02)
174.	C_6H_{14}	Isohexane (70) (18)	268.5	299.6	332.0	366.6	403.4	482.0					(1.01) − 1.00
175.	C_6H_{14}	2,2-Dimethyl butane (18)	209.6	237.2	266.7	303.0							1.09 − 1.07
176.	C_6H_{14}	3-Methyl pentane (18)	253.8	280.4	309.7	342.5							(1.01) −(1.03)
177.	$C_6H_{14}O$	Hexyl alcohol (26)			18.5	27.0	36.3						(1.80) − 1.68
178.	$C_6H_{14}O$	Ethyl isobutyl ether (70)	206.8	234.5	263.4	294.2	327.2	397.2	473.7				(1.04) −(1.03)
179.	$C_6H_{14}O$	*n*-Propyl ether (70)	184.6	209.7	237.4	265.9	295.5	359.8	431.3				(1.07) −(1.06)
180.	$C_6H_{14}S$	*n*-Hexyl mercaptan (6)	89.65	105.3	121.6	138.6	156.1	193.9	235.0	279.1			(1.05) −(1.07)
181.	$C_6H_{14}S$	Hexane thiol-2 (6)	106.7	125.0	143.1	162.1	182.0	223.8	269.7	319.6			(1.01) −(1.03)
182.	$C_6H_{15}N$	Triethyl amine (28) (55) (3.5)	214.8	242.5	271.4	301.7	333.3	401.4	474.4				(1.24) −(1.34)
						271.7$_{25}$°							
183.	$C_6H_{15}O_4P$	Triethyl orthophosphate (29.05)				59.67	70.67	82.44					
184.	$C_7H_5F_3$	Benzotrifluoride (68.5)			174.2	195.3	216.1	258.2					1.10
185.	C_7H_5N	Phenyl cyanide (13)	51.0	61.9	75.2	88.3	101.7	130.4	160.8	194.6			(1.29) −(1.64)
186.	C_7H_5NS	Phenyl thiocyanide (48)			65.4	77.3	89.8						(1.17) − 1.25
187.	C_7H_5NS	Phenyl isothiocyanide (5)	43.65	53.91	64.28	75.48	88.03	113.8	140.2	168.1			1.18 −(1.33)
188.	C_7H_7Br	*o*-Bromotoluene (6.5)	45.29	55.40	66.14	77.45	89.36	114.45	141.63	170.58			(1.08) −(1.06)
189.	C_7H_7Br	*m*-Bromotoluene (6.5)	57.84	68.83	80.34	92.34	104.76	130.87	158.78	188.22			1.02 −(1.02)
190.	C_7H_7Br	*p*-Bromotoluene (6.5)				91.31	103.72	130.27	158.73	188.31			1.02 −(1.02)
191.	C_7H_7Cl	*o*-Chlorotoluene (6.5)	71.28	84.14	97.80	112.01	126.69	157.78	191.50	227.88			1.11 − 1.12
192.	C_7H_7Cl	*m*-Chlorotoluene (6.5)	84.87	98.83	114.02	130.88	146.91	181.23	217.14	255.11			1.07 − 1.07
193.	C_7H_7Cl	*p*-Chlorotoluene (6.5)		96.88	112.04	127.50	143.35	177.23	213.41	251.58			1.07 − 1.08
194.	C_7H_7F	*o*-Fluorotoluene (68.5)			147.1	166.6	186.2	230.5					(1.15) − 1.18
195.	C_7H_7F	*m*-Fluorotoluene (68.5)			164.5	186.6	207.9	252.7					(1.11) − 1.14
196.	C_7H_7F	*p*-Fluorotoluene (68.5)			160.9	181.0	202.1	247.					(1.12) − 1.15
197.	$C_7H_7NO_2$	*o*-Nitrotoluene (6.5)	26.08	33.83	42.25	51.44	61.28	82.78	106.37	131.85			1.41 − 1.53
198.	$C_7H_7NO_2$	*m*-Nitrotoluene (6.5)			42.87	52.45	62.61	84.62	108.55	134.01			1.41 − 1.52
199.	$C_7H_7NO_2$	*p*-Nitrotoluene (6.5)						83.43	106.68	131.98			1.53
200.	C_7H_8	Toluene (70)	129.7	149.3	170.2	191.7	214.0	261.9	313.6	370.3			(1.16) −(1.14)

TABLE XXV. (*Continued.*)

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	π
201.	C_7H_8O	Benzyl alcohol (66)			16.5	23.1	30.4	48.1					(1.69) – (1.64)
202.	C_7H_8O	*o*-Cresol (16)	2.52	5.6	10.5	16.3	24.4	44.6	69.9	98.0			1.75 – 1.56
203.	C_7H_8O	*m*-Cresol (16)	1.18	2.89	5.92	10.6	16.9	33.4	55.6	83.5			1.81 – 1.60
204.	C_7H_8O	*p*-Cresol (16)	1.02	2.53	5.29	9.52	15.3	30.5	51.8	78.4			1.82 – 1.62
205.	C_7H_9N	Benzyl amine (55)			57.	69.	83.	111.	141.	173.	208.		(1.55) – (1.70)
206.	C_7H_9N	Methyl aniline (13)	23.0	32.6	43.4	55.2	68.2	97.4	128.9				(1.44) – (1.71)
207.	C_7H_9N	*o*-Toluidine (13)	9.4	15.6	22.8	31.3	41.0	63.4	90.2	120.3			(1.54) – (1.83)
208.	C_7H_9N	*m*-Toluidine (11)	11.55	18.13	26.28	35.88	46.59	71.46	99.59	130.0			(1.52) – (1.80)
209.	C_7H_9N	*p*-Toluidine (69) (55) (16)					48.2	72.0	99.2	129.0	158.0	188.0	1.70 – (1.84)
210.	$C_7H_{11}F_3$	Trifluoromethyl cyclohexane (68.5)			105.1	120.6	136.3	173.9					(1.22)
211.	$C_7H_{12}O$	*o*-Methyl cyclohexanone (33)			58.4	70.6	83.8	111.9					1.37 – 1.35
212.	$C_7H_{12}O$	*m*-Methyl cyclohexanone (33)			58.3	70.4	83.0	109.5					1.37 – 1.36
213.	$C_7H_{12}O$	*p*-Methyl cyclohexanone (33)			58.2	70.2	82.0	107.0	131.7				1.37 – 1.37
214.	C_7H_{14}	Methyl cyclohexane (18)	102.5	119.0	138.0	159.5							1.20 – (1.18)
215.	$C_7H_{14}O$	*o*-Hexahydrocresol (33) (72)			4.59	8.0	14.8	32.6	60.0	101.0			(1.84) – (1.55)
216.	$C_7H_{14}O$	*m*-Hexahydrocresol (72)			4.35								
217.	$C_7H_{14}O$	*p*-Hexahydrocresol (72)			3.26								
218.	$C_7H_{14}O_2$	α-Ethyl-valeric acid (69)			22.	30.	39.	57.					(1.53) – 1.45
219.	$C_7H_{14}O_2$	*n*-Heptylic acid (6) (31) (23)		17.80	23.06	29.39	36.52	52.88	72.39	94.65	122.0		(1.49) – 1.49
220.	$C_7H_{14}O_2$	Ethyl *n*-valerate (5)	87.17	103.5	120.2	138.1	157.4	198.5	241.5	289.4			1.11 – 1.15
221.	$C_7H_{14}O_2$	*n*-Butyl propionate (5)	86.58	102.6	119.7	137.7	156.4	196.3	242.1	291.1			1.11 – 1.14
222.	$C_7H_{14}O_2$	*n*-Propyl *n*-butyrate (31)			120.5								(1.12)
223.	$C_7H_{15}F$	*n*-Heptyl fluoride (68.5)			159.9	180.8	203.4	250.2					1.15
224.	C_7H_{16}	*n*-Heptane (70)	191.8	216.8	242.9	270.4	298.6	361.0	429.7				(1.03) – 1.02
225.	C_7H_{16}	Isoheptane (70)	208.8	235.5	263.1	292.5	322.3	387.8	461.8				(1.01) – 0.99
226.	$C_7H_{16}O$	*n*-Heptyl alcohol (6) (26)	10.00	13.12	18.47	25.19	33.44	55.01	84.28	121.5	168.2	222.0	1.64 – 1.44
227.	$C_7H_{16}O$	Triethyl carbinol (5)	3.104	7.291	14.82	26.69	43.18	88.45	145.0	212.6			1.73 – 1.30
228.	$C_7H_{16}S$	*n*-Heptyl mercaptan (6)	67.70	80.97	94.70	109.6	125.2	158.4	195.0	234.3			(1.04) – (1.06)
229.	$C_7H_{16}S$	Heptane thiol-2 (6)	80.70	95.67	111.5	128.2	145.3	182.9	219.6	267.8			(1.00) – (1.02)
230.	C_7H_8O	Acetophenone (17) (45) (58) (39)			54.0	64.5			126.5				1.28 – (1.29)
231.	C_8H_9FO	*o*-Fluorophenetol (68.5)			65.7	79.95	94.61						(1.23) – (1.21)
232.	C_8H_9FO	*m*-Fluorophenetol (68.5)			76.00	91.5	107.3	142.1					(1.20) – (1.18)
233.	C_8H_9FO	*p*-Fluorophenetol (68.5)			74.5	89.8	105.2	139.8					(1.20) – (1.18)
234.	C_8H_{10}	Ethyl benzene (70)	114.3	131.5	149.5	168.3	188.4	230.9	277.1	326.7			(1.10) – 1.10
235.	C_8H_{10}	*o*-Xylene (70)	90.2	106.6	123.5	141.4	160.1	199.8	243.0	288.7	338.8	392.8	(1.17) – (1.14)
236.	C_8H_{10}	*m*-Xylene (70)	124.2	142.7	161.7	182.2	202.7	247.0	293.5	344.8	398.8		(1.08) – (1.09)
237.	C_8H_{10}	*p*-Xylene (70)		135.8	154.9	174.8	196.0	240.1	288.8	341.3	396.8		(1.11) – (1.09)
238.	$C_8H_{10}O$	2-Phenyl ethyl alcohol (5)	2.256	4.204	7.013	11.13	16.37	30.72	49.71	74.6			1.70 – 1.51
239.	$C_8H_{10}O$	Benzyl methyl ether (69)					89.						(1.24)
240.	$C_8H_{10}O$	Phenetol (16) (69) (31) (41)	53.8	65.5	79.3	95.0	111.3	145.6	179.2				1.20 – 1.20
241.	$C_8H_{11}N$	Dimethyl aniline (13) (16)	49.0	59.2	70.8	83.3	96.5	125.0	155.8	190.0			(1.23) – (1.51)
242.	$C_8H_{11}N$	Ethyl aniline (13)	24.3	33.6	44.5	56.6	69.7	98.7	130.6	165.8			(1.36) – (1.56)
243.	$C_8H_{11}NO$	*o*-Phenetidine (6.5)	6.058	10.58	16.45	23.69	32.02	51.81	75.03	100.71			1.55 – 1.61
244.	$C_8H_{11}NO$	*m*-Phenetidine (6.5)				7.738	12.61	26.33	44.73	66.75			1.67 – (1.73)
245.	$C_8H_{11}NO$	*p*-Phenetidine (6.5)			7.751	12.05	17.82	32.66	51.50	73.12			1.64 – (1.61)
246.	$C_8H_{16}O_2$	*n*-Caprylic acid (26) (31)			17.40	23.7	30.7	45.5	65.0	90.3			(1.47) – 1.41
247.	$C_8H_{16}O_2$	*n*-Butyl *n*-butyrate (5)	69.40	83.65	98.72	114.7	131.6	168.4	209.0	253.2			1.08 – (1.11)
248.	C_8H_{18}	*n*-Octane (70)	141.7	162.9	185.3	208.5	232.9	285.5	343.3	407.8	480.6		(1.18) – (1.02)
249.	$C_8H_{18}O$	*n*-Octyl alcohol (4)	4.803	7.436	11.03	15.73	21.79	38.46	62.20	93.54			1.65 – (1.37)
250.	$C_8H_{18}O$	Octanol-2 (4)	4.483	7.676	12.49	19.13	27.76	51.47	84.44	126.0			1.64 – (1.28)

TABLE XXV. (*Continued.*)

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	n
251.	$C_8H_{18}O$	Octanol-3 (4)	15.06	22.40	31.82	43.33	57.14	91.25	133.7	184.1			(1.50) – (1.21)
252.	$C_8H_{18}O$	Octanol-4 (4)	6.423	10.89	17.20	25.68	36.87	67.24	109.1	160.5			1.60 – (1.22)
253.	$C_8H_{18}O$	2-Methyl heptanol-1 (4)	11.97	17.96	25.52	34.79	45.86	73.63	109.8	153.9			1.53 – (1.24)
254.	$C_8H_{18}O$	2-Methyl heptanol-2 (4)	11.00	17.19	25.38	35.92	48.94	82.76	127.5	185.0			1.54 – (1.19)
255.	$C_8H_{18}O$	2-Methyl heptanol-3 (4)	2.927	5.981	11.07	18.88	29.90	62.42	107.9	162.7			1.65 – (1.21)
256.	$C_8H_{18}O$	2-Methyl heptanol-4 (4)	3.407	6.005	10.60	17.58	27.48	57.99	103.1	160.0			1.66 – (1.19)
257.	$C_8H_{18}O$	2-Methyl heptanol-5 (4)	37.88	49.69	63.25	79.13	96.68	137.8	187.1	242.4			(1.36) – (1.15)
258.	$C_8H_{18}O$	2-Methyl heptanol-6 (4)	6.452	10.85	17.00	25.05	35.14	61.96	98.15	143.6			1.60 – (1.26)
259.	$C_8H_{18}O$	2-Methyl heptanol-7 (4)	4.376	6.940	10.45	15.15	21.25	38.18	62.70	95.39			1.66 – (1.35)
260.	$C_8H_{18}O$	3-Methyl heptanol-1 (4)	28.04	37.28	47.89	59.98	73.65	105.7	144.5	190.0			(1.40) – (1.21)
261.	$C_8H_{18}O$	3-Methyl heptanol-2 (4)	32.35	42.43	56.17	70.74	87.03	124.6	168.4	217.6			(1.38) – (1.18)
262.	$C_8H_{18}O$	3-Methyl heptanol-3 (4)	5.033	9.429	16.17	25.70	38.38	73.73	120.6	175.7			1.61 – (1.20)
263.	$C_8H_{18}O$	3-Methyl heptanol-4 (4)	23.79	33.68	45.59	59.77	76.03	113.8	160.3	211.0			(1.45) – (1.18)
264.	$C_8H_{18}O$	3-Methyl heptanol-5 (4)	48.54	62.02	76.95	93.52	111.7	151.9	198.2	249.7			(1.32) – (1.15)
265.	$C_8H_{18}O$	3-Methyl heptanol-6 (4)	21.44	29.77	39.86	51.76	65.60	98.35	139.3	190.6			(1.44) – (1.19)
266.	$C_8H_{18}O$	3-Methyl heptanol-7 (4)	7.201	11.07	16.20	22.84	31.05	52.77	82.21	119.9			1.59 – (1.29)
267.	$C_8H_{18}O$	4-Methyl heptanol-1 (4)	15.29	21.78	29.58	39.04	49.99	76.89	112.5	156.1			1.50 – (1.24)
268.	$C_8H_{18}O$	4-Methyl heptanol-2 (4)	12.95	19.34	27.50	37.68	50.00	81.72	123.5	174.7			1.52 – (1.21)
269.	$C_8H_{18}O$	4-Methyl heptanol-3 (4)	52.63	66.97	83.30	101.3	121.	165.0	214.0	267.0			(1.32) – 1.13
270.	$C_8H_{18}O$	4-Methyl heptanol-4 (4)	3.095	6.556	12.34	21.20	33.75	70.94	122.9	184.4			1.64 – (1.18)
271.	$C_8H_{18}O$	2-Ethyl hexanol-1 (4)	4.814	8.199	12.98	19.44	27.69	50.43	82.03	122.8			1.63 – (1.28)
272.	$C_8H_{18}O$	*n*-Butyl ether (11)	106.1	124.5	144.5	164.9	186.4	233.2	285.7	341.2			(1.06) – (1.05)
273.	$C_8H_{18}O$	Ethyl hexyl ether (26)			99.	116.	125.	173.					1.14 – (1.14)
274.	$C_8H_{18}S$	*n*-Octyl mercaptan (6)	50.70	61.78	73.78	86.43	100.3	129.7	161.6	198.7			1.04 – (1.05)
275.	$C_8H_{18}S$	Octane thiol-2 (6)	60.39	73.18	86.88	101.4	116.6	149.6	185.9	223.7			1.00 – (1.01)
276.	C_9H_7N	Quinoline (16) (42)		21.0	27.3	34.1	42.0	60.0	80.0	100.0	121.8	145.3	(1.33) – 1.58
277.	$C_9H_{10}O_2$	Ethyl benzoate (31) (41) (63) (39) (40)			44.7	55.0	66.2	91.1					1.18 – 1.17
278.	$C_9H_{10}OS$	Ethyl thiobenzoate (60)				*41.3*$_{25}$°							(1.05)
279.	$C_9H_{12}O$	β-Phenylpropyl alcohol (24)				8.5	13.5	*19.1*$_{50}$°					1.65
280.	$C_9H_{13}N$	Ethyl-*o*-toluidine (55) (69)			43.6	56.2	69.5	98.0					1.38 – 1.42
281.	$C_9H_{13}N$	Ethyl-*p*-toluidine (69)				48.0	61.4	90.0					1.41 – (1.44)
282.	$C_9H_{18}O$	Di-*n*-butyl ketone (3.5)			76.69	90.33	104.8	136.0	170.0	206.8			1.12 – 1.14
283.	$C_9H_{18}O_2$	*n*-Butyl *n*-valerate (5)	55.87	68.20	81.40	95.48	110.4	143.2	179.9	219.5			1.06 – 1.07
284.	$C_9H_{18}O_2$	Isobutyl *n*-valerate (26)				*99.0*$_{25}$°							(1.03)
285.	$C_9H_{18}O_2$	Ethyl *n*-heptylate (5)	54.62	66.85	79.97	93.97	108.7	141.8	178.1	217.1			1.06 – 1.08
286.	$C_9H_{18}O_2$	*n*-Heptyl acetate (5)	43.06	53.94	65.80	78.51	92.02	120.7	153.1	187.0			1.10 – 1.13
287.	$C_9H_{18}O_2$	*n*-Amyl *n*-butyrate (5)	56.34	68.88	82.42	96.82	112.2	145.4	183.7	224.0			1.06 – 1.07
288.	$C_9H_{18}O_2$	Methyl octoate (26)			71.7	86.7	102.3						(1.10) – 1.08
289.	$C_9H_{18}O_2$	Pelargonic acid (31) (23)			12.4	16.2	20.8	33.6	49.4	67.0			1.43 – (1.42)
290.	C_9H_{20}	*n*-Nonane (6)	103.2	121.3	140.7	161.3	182.5	228.2	278.1	334.8			(1.21) – (1.01)
291.	$C_9H_{20}S$	*n*-Nonyl mercaptan (6)	39.00	48.83	59.48	71.08	83.24	109.8	139.1	171.0	205.3		1.02 – (1.04)
292.	$C_9H_{20}S$	Nonane thiol-2 (6)	44.77	55.63	67.49	80.14	93.55	122.6	155.2	190.4	229.9		1.00 – (0.99)
293.	$C_9H_{21}O_4P$	Tri-*n*-propyl orthophosphate (29.05)			35.30	44.52	54.47						
294.	$C_{10}H_8$	Naphthalene (45) (44)							112.9	154.			1.23
295.	$C_{10}H_{12}$	Tetrahydronaphthalene (69) (35)			45.0	54.8	65.0	89.8	117.8				1.24 – 1.22
296.	$C_{10}H_{12}O$	Phenyl propyl ketone (5)	24.57	32.97	42.33	52.82	64.08	88.35	115.6	144.7			1.18 – 1.17
297.	$C_{10}H_{12}O_2$	Eugenol (11)	3.465	6.563	10.96	16.69	23.72	41.15	62.76	86.71			1.39 – 1.25
298.	$C_{10}H_{15}N$	Diethyl aniline (13)	25.5	35.1	45.8	57.5	70.2	97.9	128.7	162.1			(1.20) – (1.34)
299.	$C_{10}H_{18}$	Decahydronaphthalene (35)				45.3	53.7	73.9	99.1				1.28 – 1.26
300.	$C_{10}H_{20}O$	Menthol (37) (65)					6.0	20.4	50.0	99.0			1.64 – 1.27

TABLE XXV. (*Continued.*)

No.	Formula	Name	0	10	20	30	40	60	80	100	120	140	n
301.	$C_{10}H_{20}O_2$	Ethyl *n*-caprylate (26)			65.6	79.0	92.8						(1.05) – 1.04
302.	$C_{10}H_{20}O_2$	*n*-Capric acid (26)					18.3	28.3	41.0				(1.40) – (1.37)
303.	$C_{10}H_{22}$	*n*-Decane (6)	77.98	93.42	109.8	127.5	146.0	186.1	230.2	278.4			(1.21) – (1.01)
304.	$C_{10}H_{22}$	2,7-Dimethyl octane (15)			120.8	139.3	159.1	201.4					(1.00) – 1.00
305.	$C_{10}H_{22}O$	Di-*n*-amyl ether (11)	63.24	77.34	92.40	108.2	125.2	162.0	203.0	246.2			(1.14) – (1.02)
306.	$C_{10}H_{22}O$	Di-iso-amyl ether (11)	68.40	83.17	98.80	115.5	133.1	171.5	214.0	260.7			(1.13) – (1.00)
307.	$C_{11}H_{24}$	*n*-Undecane (6)	58.00	71.12	85.32	100.4	115.7	151.1	189.6	230.0			(1.19) – (1.00)
308.	$C_{12}H_{10}$	Diphenyl (6)						$67.18_{70}°$	80.48	103.0			(1.22) – 1.17
309.	$C_{12}H_{11}N$	Diphenyl amine (69) (16) (55)						23.2	38.5	59.0	83.3		1.40 – 1.40
310.	$C_{12}H_{24}O_2$	Lauric acid (6)					11.1	18.63	28.49	40.70	55.90	74.05	160°C/96.00
													1.35 – 1.27
311.	$C_{12}H_{26}$	*n*-Dodecane (6)	43.50	54.69	66.98	78.93	91.62	122.9	157.2	195.4			(1.17) – 1.00
312.	$C_{12}H_{27}N$	Tri-*n*-butyl amine (11)	44.70	57.36	70.96	85.72	101.3	135.9	174.4	216.2			(1.05) – (1.09)
313.	$C_{12}H_{27}O_4P$	Tri-*n*-butyl orthophosphate (29.05)			25.74	33.10	41.03						
314.	$C_{13}H_{10}O$	Benzophenone (45) (50)				9.1	13.2	25.2	41.6	63.4			1.36 – (1.16)
315.	$C_{13}H_{12}$	Diphenyl methane (45)								120.			(1.07)
316.	$C_{13}H_{13}N$	Methyl diphenyl amine (16)		9.5	13.7	19.4	26.0	40.2	57.5	80.0	107.5		(1.19) – (1.26)
317.	$C_{13}H_{26}O_2$	Methyl laurate (26)				36.0	44.5						1.02
318.	$C_{14}H_{12}O_2$	Benzyl benzoate (41) (9) (40)		6.5	10.0	14.1	19.1	30.7	44.5	60.4			1.18 – (1.10)
319.	$C_{14}H_{14}O$	Benzyl ether (11)	9.497	13.79	18.75	24.62	31.19	46.20	63.75	83.31			1.17 – (1.06)
320.	$C_{14}H_{28}O_2$	Myristic acid (23) (26)						13.5	21.6	31.4			(1.29) – (1.23)
321.	$C_{14}H_{28}O_2$	Ethyl laurate (26)				36.8	46.6	69.0					0.96 – (0.95)
322.	$C_{15}H_{33}N$	Tri-*n*-amyl amine (11)	21.20	29.13	38.22	48.50	59.90	85.31	114.7	146.9			(1.00) – (1.01)
323.	$C_{15}H_{33}N$	Tri-iso-amyl amine (11)	20.07	27.95	37.11	47.62	58.99	85.25	115.2	148.5			(1.00) – (0.99)
324.	$C_{16}H_{32}O_2$	Palmitic acid (23)						9.2	16.4	23.9			1.25
325.	$C_{16}H_{34}O$	Cetyl alcohol (5)						12.03	21.96	36.38			1.29 – 1.13
326.	$C_{16}H_{34}O$	2-Ethyl-tetradecanol (12)			2.628	4.322	6.707	14.23	26.40	43.68			1.27 – 1.10
327.	$C_{16}H_{34}O$	2-Propyl-tridecanol (12)			2.792	4.574	7.109	15.22	28.24	46.32			1.27 – 1.09
328.	$C_{16}H_{34}O$	2-Butyl-dodecanol (12)			2.469	4.100	6.452	14.21	26.98	45.50			1.27 – 1.10
329.	$C_{16}H_{34}O$	2-Amyl-undecanol (12)			2.539	4.177	6.569	14.36	27.07	46.17			1.27 – 1.09
330.	$C_{16}H_{34}O$	2-Hexyl-decanol (12)			2.413	3.978	6.308	13.96	26.81	45.80			1.28 – 1.09
331.	$C_{16}H_{34}O$	2-Heptyl-nonanol (12)			2.453	4.040	6.360	13.99	27.01	46.04			1.28 – 1.09
332.	$C_{18}H_{36}O_2$	Ethyl palmitate (26)			14.8	20.0	25.7	38.2					(0.99) – (0.90)
333.	$C_{18}H_{36}O_2$	Stearic acid (6)			$78.0_{180}°$		$92.0_{200}°$	$8.61_{870}°$	12.58	19.55	29.70	41.96	160°C/56.09
													1.21 – 1.07
334.	$C_{18}H_{36}O_2$	Cetyl acetate (12)			12.81	17.05	22.30	34.46	49.01	68.08			0.99 – 0.88
335.	$C_{18}H_{36}O_2$	2-Methyl-pentadecyl acetate (12)	6.381	9.569	13.49	18.21	23.69	36.82	52.62	70.52			0.99 – 0.89
336.	$C_{18}H_{36}O_2$	2-Ethyl-tetradecyl acetate (12)	6.620	9.275	13.36	18.11	23.75	37.30	53.65	72.30			0.99 – 0.89
337.	$C_{18}H_{36}O_2$	2-Propyl-tridecyl acetate (12)	6.305	9.690	13.97	19.18	25.24	39.85	57.44	77.07			0.99 – 0.87
338.	$C_{18}H_{36}O_2$	2-Butyl-dodecyl acetate (12)	6.020	9.394	13.65	18.87	24.47	39.76	57.77	78.26			0.99 – 0.87
339.	$C_{18}H_{36}O_2$	2-Amyl-undecyl acetate (12)	6.040	9.376	13.64	18.89	25.03	39.79	57.62	78.52			0.99 – 0.87
340.	$C_{18}H_{36}O_2$	2-Hexyl-decyl acetate (12)	6.099	9.485	13.84	19.15	25.42	40.69	59.09	80.67			0.99 – 0.86
341.	$C_{18}H_{36}O_2$	2-Heptyl-nonyl acetate (12)	6.034	9.373	13.65	18.88	25.06	40.00	58.35	79.47			0.99 – 0.87
342.	$C_{19}H_{16}$	Triphenyl methane (45)							21.	31.1			(1.22) – (1.09)
343.	$C_{20}H_{40}O_2$	Ethyl stearate (3)				15.29	19.82	$24.89_{50}°$					(0.96) – (0.89)
344.	$C_{21}H_{21}O_4P$	Tri-*o*-tolyl phosphate (6) (29.05)			0.775	1.639	3.048	7.421	14.00				
345.	$C_{22}H_{34}O_2$	Ethyl abietate (6)			0.1119		0.7109	2.520	6.222				
346.	$C_{25}H_{50}O_2$	Undecane-β-ol myristate (26)				$8.1_{25}°$							(0.85)

TABLE XXVI. *Association of normal compounds.*

Group A	Average percent
Monohydroxy alcohols at 200 rhes $n=2.139-0.097N_c$	Deviation 1.71
Monobasic acids at 100 rhes $n=1.789-0.042N_c+0.490(HCOOH)$ $+0.172(CH_3.COOH)$	1.05
Esters at 200 rhes $n=1.391-0.0346N_c$	1.74
Thio-alcohols at 200 rhes $n=1.110-0.0084N_c-0.040N_2(SH)$	0.54
Group B	
Ketones	$n=1.403-0.040N_c$
Monochlorides	$n=1.161-0.013N_c$
Ethers	$n=1.123-0.012N_c$
Hydrocarbons	$n=1.072-0.006N_c$
Monobromides	$n=1.052-0.004N_c$
Monoiodides	$n=1.034-0.003N_c$

the association formulas of Bingham, Darrall and Fornwalt for the normal compounds as given in Table XXVI Group A. Approximate formulas have been derived for the classes of normal compounds given in Table XXVI Group B. In this table, n is the association factor, N_c is the number of carbon atoms, the terms containing (HCOOH) and (CH_3COOH) take care of the apparent abnormality in formic and acetic acids, and the term containing $N_2(SH)$ is the constitutional correction for the SH group in the secondary position. In each of these ten classes of compounds the association appears to decrease quite linearly with the number of carbon atoms.

2. The normal compound with the associating group at the end of the chain is more highly associated than the corresponding (secondary) compound with the associating group brought toward the center of the chain. This is illustrated by the associations of the following octyl alcohols:

Octanol-1	$n=1.462$ at 100 rhes
Octanol-2	$n=1.400$ at 100 rhes
Octanol-3	$n=1.309$ at 100 rhes

Normal and secondary mercaptans also illustrate this generalization.

3. An iso-grouping in the hydrocarbon residue brings about a decrease in the association.[d] Numerous examples may be found to prove this statement. Isohexane, isoheptane, isopropyl chloride, isopropyl bromide, isopropyl iodide, isooctyl alcohol, isobutyl alcohol, isobutyric acid, di-iso-amyl ether, and many others are all less associated than the corresponding normal compounds.

4. The decrease in association caused by an iso-grouping is still further accentuated by moving the iso grouping toward the center of the chain or toward the associating group.[d] An example of this is the trend of association found in the following octyl alcohols:

Octanol-1	$n=1.462$ at 100 rhes
2-Methyl heptanol-7	$n=1.457$ at 100 rhes
3-Methyl heptanol-7	$n=1.409$ at 100 rhes
4-Methyl heptanol-1	$n=1.346$ at 100 rhes
3-Methyl heptanol-1	$n=1.279$ at 100 rhes

and also:

Inactive amyl alcohol	$n=1.617$ at 200 rhes
Active amyl alcohol	$n=1.606$ at 200 rhes

5. The association is still further decreased by clustering alkyl residues around the associating groups.[d] This is illustrated at 200 rhes as follows:

n-Butyl alcohol	$n=1.732$
tert.-Butyl alcohol	$n=1.660$

and

iso-Amyl alcohol	$n=1.617$
tert.-Amyl alcohol	$n=1.530$

6. In the class of esters it is found, as might be expected, that methyl formate is the most associated of all esters; furthermore, methyl esters are all associated as well as are all formates, but the esters of the higher alcohols united to acids above butyric acid appear to be very slightly associated. The theory of protection advanced by Bingham and Fornwalt[6] enables one to estimate the relative association of the various esters. The effect of a methylene group is in general quite different, dependent upon whether it is placed in the acid or in the alcoholic residue; the effect in either case is not a linear function of the number of carbon atoms. This effect is now being studied by Bingham and DeTurck;[e] and it is believed that a logarithmic relationship exists between the association of the esters and the number of carbon atoms. The logarithmic curves give very accurate results, but for practical purposes, a linear curve may be used with approximate accuracy.

[d] For qualifications see p. 397 (15A).

[e] Bingham and DeTurck, J. Rheology 3, 479 (1933).

7. Compounds with two associating groups are more highly associated than the corresponding compounds with only one associating group. For example:

Ethylene bromide	$n = 1.114$ at 200 rhes
Ethyl bromide	$n = 1.020$ at 200 rhes
Ethylene glycol	$n = 2.538$ at 100 rhes
Ethyl alcohol	$n = 2.016$ at 100 rhes
Ethyl lactate	$n = 1.432$ at 200 rhes
Ethyl propionate	$n = 1.182$ at 200 rhes

8. Compounds with two associating groups are most highly associated when these groups are separated as far as possible: and least associated when attached to the same carbon atom. For example:

Ethylidine chloride	$n = 1.110$ at 200 rhes
Ethylene chloride	$n = 1.284$ at 200 rhes

This probably explains the fact that acids are less associated than the corresponding alcohols, which otherwise appears to be an exception to the seventh generalization.

9. Unsaturated compounds are less associated than the corresponding saturated compounds. For example:

Allyl alcohol	$n = 1.779$ at 200 rhes
Propyl alcohol	$n = 1.869$ at 200 rhes
Allyl bromide	$n = 1.026$ at 200 rhes
Propyl bromide	$n = 1.040$ at 200 rhes
Benzene	$n = 1.284$ at 100 rhes
Cyclohexane	$n = 1.395$ at 100 rhes

Cyclic compounds however, are habitually more highly associated than the corresponding fully saturated compounds. For example:

Cyclohexane	$n = 1.395$ at 100 rhes
n-Hexane	$n = 1.030$ at 100 rhes
Thiophene	$n = 1.154$ at 100 rhes
n-Butyl mercaptan	$n = 1.071$ at 100 rhes

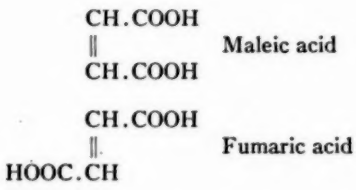
10. In aromatic compounds in which two non-associating alkyl residues are attached to the benzene ring, the para compounds are less associated than the ortho compounds. For example:

o-Xylene	$n = 1.146$ at 200 rhes
p-Xylene	$n = 1.083$ at 200 rhes
Benzene	$n = 1.258$ at 200 rhes

It is obvious that the benzene ring is better protected when the methyl groups are in the para position than when they are in the ortho position. It would then seem logical to expect the meta compound, on the basis of protection, to have an association midway between that of the ortho and para, but actually its factor is 1.073 at 200 rhes.

11. On the other hand, if the aromatic compound contains two associating groups, the para compound should be most highly associated and the ortho compound, least associated, as would be expected from the eighth generalization. But data here are lacking because of the fact that most of the compounds of this type are solids at ordinary temperatures.

12. By the same reasoning one can explain why maleic acid is less associated than fumaric acid.



13. In aromatic compounds in which one alkyl residue and one associating group are attached to the benzene ring, the presence of the alkyl residue in the ortho position to the associating group is most effective in lowering the association, as would be expected on the basis of protection, and in the para position it is least effective. For example:

o-Cresol	$n = 1.560$ at 100 rhes
m-Cresol	$n = 1.603$ at 100 rhes
p-Cresol	$n = 1.618$ at 100 rhes
o-Methyl cyclohexanone	$n = 1.354$ at 100 rhes
m-Methyl cyclohexanone	$n = 1.359$ at 100 rhes
p-Methyl cyclohexanone	$n = 1.366$ at 100 rhes
Ethyl *o*-Toluidine	$n = 1.418$ at 100 rhes
Ethyl *p*-Toluidine	$n = 1.439$ at 100 rhes
o-Toluidine	$n = 1.798$ at 100 rhes
m-Toluidine	$n = 1.766$ at 100 rhes
p-Toluidine	$n = 1.767$ at 100 rhes

o-Toluidine shows an exception to this generalization, being slightly more highly associated than the meta and para compound. This needs further investigation.

14. The foregoing studies have suggested a classification of associating groups in the order of their ability to accentuate association. A tentative arrangement of these groups is as follows

1. Amines RNH_2	7. Ketones RCO.R
2. Alcohols ROH	8. Chlorides RCl
3. Acids RCOOH	9. Ethers ROR
4. Acid anhydrides RCO.O.OCR	10. Thiols RSH
5. Aldehydes RCHO	11. Bromides RBr
6. Esters RCOOR	12. Iodides RI
	13. Hydrocarbons RCH_3

Data which indicate this arrangement are as follows:[f]

at 100 rhes:	*n*
Aniline	1.971
Phenol	1.705
at 200 rhes:	
n-Propyl alcohol	1.869
Propionic acid	1.731
Propionaldehyde	1.366
Ethyl formate	1.310
Methyl acetate	1.288
Acetone	1.283
Propyl chloride	1.122
Propyl mercaptan	1.090
Propyl bromide	1.040
Propyl iodide	1.025
Di-*n*-butyl ether	1.050
Octyl mercaptan	1.042
n-Octane	1.031
Butyl alcohol	1.732
Butyric acid	1.657
Acetic anhydride	1.410
Propyl formate	1.283
Methyl ethyl ketone	1.282
Methyl propionate	1.236
Ethyl acetate	1.232
Di-propyl ether	1.071
Hexyl mercaptan	1.064
n-Hexane	1.027

More data are being sought to make this comparison more direct. There is no direct method, for instance, of comparing the association of the hydrocarbons with that of the bromides and iodides. But there is reason to believe that all halogens accentuate association to some extent, while it is well known that a methylene group actually diminishes the association.

[f] Note: Each comparison is made using normal compounds with the same number of carbon atoms.

15. The effect of temperature on association may be discussed from two viewpoints.

(A) The effect of temperature on association depends upon the constitution of the compound. The normal compounds are most stable in retaining association; while their isomers, often having high association at low temperature, lose their association more rapidly until, at 200 rhes, for the compounds studied, conditions exist as stated in generalizations 3, 4 and 5. There is no uncertainty in this argument due to any inexactitude in the atomic temperature constants. The compounds under discussion are isomers, i.e., the calculated temperatures for each are the same, and the phenomenon is shown by the crossing of the observed fluidity-temperature curves. This phenomenon is especially well illustrated by the alcohols.

	Association at 10	50	100	200	300 rhes
n-Butyl alcohol	(1.846)	1.863	1.825	1.732	(1.648)
iso-Butyl alcohol	1.948	1.906	1.840	1.724	(1.629)
tert.-Butyl alcohol	(2.102)	1.901	1.796	1.660	(1.568)

The isomeric amyl alcohols also show the same effect, tert.-amyl alcohol having a very high temperature coefficient of association and its fluidity-temperature curve showing a marked curvature.

The octyl alcohols studied by Bingham and Darrall[4] furnish material for an interesting discussion of this phenomenon. It has been pointed out that, according to the theory of protection, 4-methyl heptanol-4 should be the least associated of the compounds studied because both of the varying groups are brought as near to the center of the molecule as possible. At 200 rhes, however, 4-methyl heptanol-3 is less associated. It should be brought out, in view of the foregoing argument, that the compounds having the hydroxyl group attached to the fourth carbon atom have a much higher temperature coefficient of association than those having the hydroxyl group attached to the third carbon atom; and that at about 400 rhes the fluidity-temperature curves will cross. Thus it seems that generalizations 3, 4 and 5 may not apply at low temperatures, in fact the conditions are reversed.

(B) The effect of temperature on the association of various classes of compounds is un-

certain as far as quantitative measurements are concerned, since it depends upon the atomic temperature constants which are uncertain at 10, and 50 as well as 500 rhes. Most compounds decrease in association as the temperature is increased. In any case, the effect of temperature is usually small. The principal exceptions to this generalization are the nitrogen compounds and thio-alcohols. The fact that these compounds do increase in association with increasing temperature does not, however, indicate that there is an error in the atomic temperature constants.

Polymerization and Condensation

Even wider uses of the viscometer than hitherto thought of open out before one. Acetaldehyde and paraldehyde serve as an example of the effect of polymerization on fluidity as contrasted with that of association on fluidity. If acetaldehyde were associated in the liquid state to three molecules, the absolute temperature required to produce a fluidity of 100 rhes would be $3\times150.2=450.6°$K.

$$3\ CH_3.CHO\rightarrow(CH_3.CHO)_3$$
$$3\times150.2=450.6°.$$

The actual temperature as obtained by considerable extrapolation is 191°K so that acetaldehyde is only associated to a slight degree ($n=1.272$).

In the process of polymerization of acetaldehyde, the compound $C_6H_{12}O_3$ is formed with the loss of three double bonds and the gain of a ring grouping. It has already been proved that a double bond or ring grouping have the same effect upon the flow as if hydrogens were present. The paraldehyde should have the same temperature for a fluidity of 100 rhes as a straight chain compound equally unassociated having the formula of $C_6H_{14}O_3$ which is 249.1°K. As a matter of fact the observed temperature is 301°K so that even paraldehyde is somewhat associated ($n=1.208$) but this is *150° lower* than would have been the case had acetaldehyde been merely associated into trimolecules.

Even though polymerization is less effective than association in lowering the fluidity, there is a third method for bringing molecules together which lowers the fluidity still less, as in the familiar condensation. Two molecules of acid condense with elimination of water.

$$2\ C_2H_5COOH\rightarrow(C_2H_5CO)_2O+H_2O$$
$$2\times209.2°=286.8°+131.6°\text{ at 200 rhes.}$$

Two molecules of alcohol condense in a similar way to form ether.

$$2\ C_3H_8O\rightarrow(C_3H_7)_2O+H_2O$$
$$2\times196.2°=260.8°+131.6°.$$

A molecule of alcohol and of acid unite to form an ester.

$$C_2H_5COOH+C_3H_7OH\rightarrow C_2H_5COOC_3H_7+H_2O$$
$$209.2°+196.2°=273.8°+131.6°.$$

In the first case the temperature is not $2\times209.2°=418.4°$ but 286.8° which is 131.6° lower than this, 131.6° being the temperature value for water. In the second case, two associated molecules would require a temperature of 392.4°K, but because of the elimination of water, the temperature is again 131.6° lower, or 260.8°K. In the third case, the temperature required is not $209.2°+196.2°=405.4°$ but 273.8° which is again 131.6° below the value calculated on the basis of union by association.

The case is somewhat different in the formation of lactones.

$$CH_3.CHOH.CH_2.CH_2.COOH\rightarrow$$
$$265.3°$$
$$CH_3.\underset{\displaystyle\llcorner\!\!-\!\!O\!\!-\!\!\lrcorner}{CH}.CH_2.CH_2.CO+H_2O.$$
$$252.3°\qquad 131.6°$$

The ring formation in this case makes up for the loss of two hydrogens so that the temperature required to produce a fluidity of 200 rhes is not 131.6° lower, but simply 13.0°, corresponding to one oxygen atom.

The above calculated values for propionic anhydride (286.8°K), propyl ether (260.8°K), and for propyl propionate (273.8°K) are not exactly the values found by experiment, 357.4°, 279.2°, and 319.3° respectively, because these substances are themselves associated. The association factors are found to be for propionic anhydride ($n=1.246$), for propyl ether ($n=1.071°$), and for propyl propionate ($n=1.166°$). These values are entirely reasonable.

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Anomalies in the Viscosity of Mineral Oils at Low Temperatures[1]

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Viscosity measurements at low temperatures show that after a temperature change an oil may require several weeks to attain an equilibrium state. Oils which show this viscosity anomaly are not truly viscous. The existence of a starting pressure called the yield value was not confirmed by experiment since the oil flows even under very slight pressure.

MINERAL oils have been studied very much less thoroughly at low temperatures than at ordinary temperatures. Numerous viscometric anomalies have been found there, but up to the present no satisfactory explanations have been developed.

Recently Erk[2] pointed out that certain oils show great variations of viscosity at low temperatures. Thus the viscosity temperature curve taken as the temperature is lowered is not comparable to the curve obtained as the temperature is raised. These two curves diverge greatly at low temperatures but converge and finally become coincident as the temperature is raised. Neither of these diverging curves represents the true viscosity (nor the apparent viscosity) of the oil; they do show, however, an anomaly in the state of the oil. The following preliminary investigations were undertaken in an attempt to determine the extent of this anomaly and its cause.

METHOD OF OPERATION AND RESULTS

Because of the enormous influence of a slight variation in temperature on the viscosity in the region considered, we attempted to maintain the temperature strictly constant for several weeks.

For convenience the temperature chosen was 0°C and an oil selected which showed the above anomalies at this temperature. We used the modified Baume-Vigneron viscometer[3] with which the aspirator pressure may be so varied as to render plasticity measurements possible. The apparatus is placed in a Dewar vessel filled with melting ice, which was renewed each day. The measurements were made twice a day, in the morning and in the evening.

The selected oil taken at ordinary temperature is put into the viscometer and cooled to 0°C. The viscosity is measured at a definite low pressure. In Fig. 1 is plotted the time of efflux of the viscometer against the time during which the oil had been maintained at 0°C. The curve shows that the viscosity increases quite rapidly at first, then more slowly and becomes constant after a comparatively long time (three weeks for this particular oil). On the other hand, if the temperature of the oil is first held at −80°C for several hours and then put into the viscometer at 0°C the viscosity curve is quite different. The time of efflux decreases rapidly at first, then tends to become horizontal and practically merges with

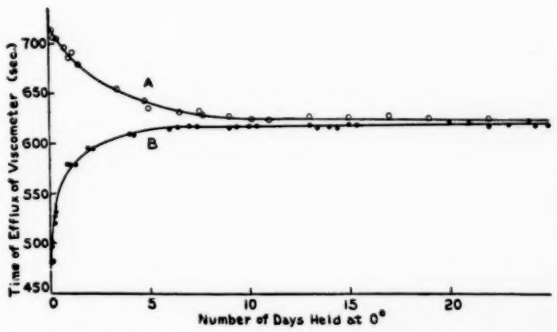

FIG. 1. Variation of viscosity with time. Curve *A* is for an oil which had been maintained at a temperature of −80°C before the test; curve *B* is for an oil which had been at room temperature.

[1] Translation from the French.

[2] Erk, Congrès du graissage, Strasbourg, 1931.

[3] Louis and de la Hitte, Congrès du graissage, Strasbourg, 1931.

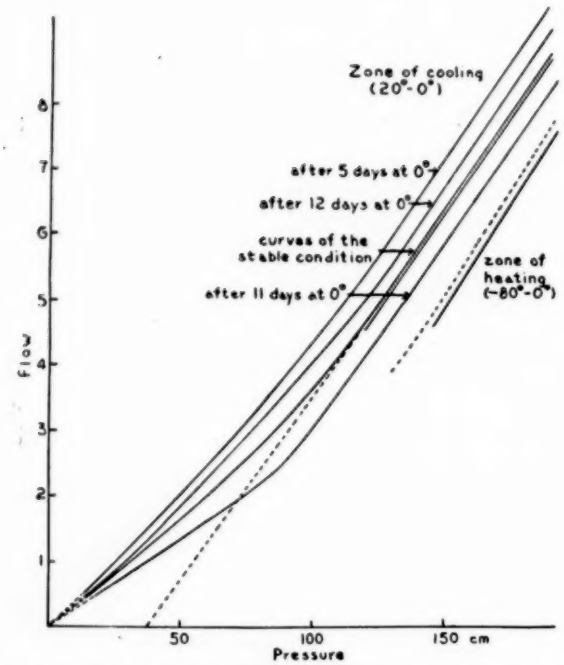

FIG. 2. Rate of flow as a function of pressure for an oil in various states of approach to equilibrium.

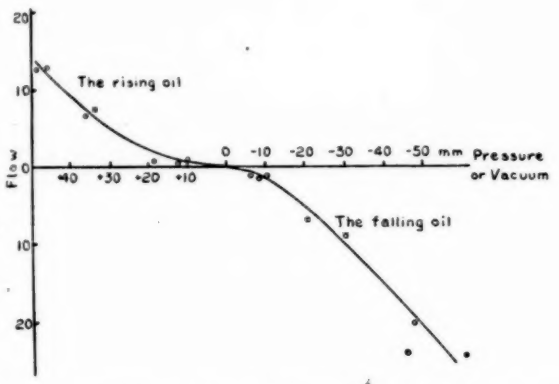

FIG. 3. Variation of flow with pressure in the low pressure range.

the preceding curve after a long time. This indicates that transformations have taken place very slowly in the oil and weeks are required for it to reach a stable state. All viscosity measurements made during the period of change are therefore deceptive. Other tests carried out under different low pressures showed that the viscosity varied within wide limits and was within the plastic or structural range.

Plasticity measurements made on oil which had reached a stable state at 0°C gave a curve which showed that the oil is very plastic. Extrapolation of the linear part shows the existence of a yield value of 39 cm of pressure. Fig. 2 gives the pressures and the flow.

Similar measurements made during the period of change gave curves which were practically parallel to the curve for the equilibrium state. They are naturally higher when the oil is approaching the equilibrium state from the higher temperature state and lower when approaching it from a low temperature state. As the change progresses the curves approach the equilibrium curve.

These anomalies explain the divergence obtained in the viscosity measurements made by the same experimenter the same day and especially at intervals of several days. We also investigated the flow under pressures so low that the plasticity equations in general do not apply. We measured the time required for filling or emptying a very small volume with a capillary tube (7.5 mm³). Instead of taking the normal volume of the bulb, we selected the smallest volume possible in order not to have to overcome too great a counterpressure and in order to be able to operate with very slight pressure. The same oil was used at 0°C as for the previous tests. The results are shown in Fig. 3 which gives the flow as a function of the pressure. As may be seen the oil moves, though slowly, even under very slight pressure. The rate of flow increases nonlinearly with the pressure.

Wall Effect in Falling Ball Method for Viscosity

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The wall effect for balls falling in a vertical cylindrical tube in a viscous fluid has been studied and expressed as an empirical function of the ratio of radii of the ball and tube. This function agrees well with observations at least to a ratio of 0.83 as compared with 0.09, the limit of agreement of Ladenburg's formula. The wall effect is probably independent of the absolute radii of the ball and tube and only slightly dependent upon the absolute viscosity. The bottom effect is negligible. For liquids of high viscosity the revised formula is

$$\eta = 2gR^2(\rho_1-\rho_2)(1-R/r)^{2.25}/9u.$$

THE falling ball method for measuring viscosity is one of the favored ones especially where absolute viscosities are desired. It has been used[2] to calibrate another method when the latter was unsuited for direct absolute readings.

As used in a vertical tube of moderate size, the method requires a modification of Stokes' equation to correct for the effect of the walls and also for the limited height of liquid. Ladenburg[3] investigated these effects and proposed the following equation:

$$\eta = \frac{2}{9}\frac{R^2g(\rho_1-\rho_2)}{u(1+2.4R/r)(1+3.3R/h)},$$

in which η is the viscosity in poises, R and r are the radii of the ball and tube in centimeters, h is the height of liquid in centimeters, $g=980$ cm per sec.^{2}, u is the observed velocity in cm per sec., and ρ_1 and ρ_2 are the densities of the ball and the liquid respectively.

In the denominator are two correction factors. The first is $(1+2.4R/r)$, which I shall designate by f_w since it is the factor correcting for wall effect. The second is $(1+3.3R/h)$ which I shall designate by f_h since it is the factor correcting for the effect of the height of the liquid. Both are empirical, but show excellent agreement with his observations in the range which he studied, in which the ratio R/r is less than 0.09 and R/h is less than 0.008. But Ladenburg's equation has been used so generally, and not always with complete recognition of the limitations in range, that it seems desirable to call attention to the serious errors that might arise; especially since some conditions, such as high viscosities or high temperatures, make it impracticable to keep within the limits studied by Ladenburg. This is especially true in the case of melted glass where relatively small tubes are necessary in order to have uniform temperature and where the ball may be used on a wire.

The wall effect can become very great with moderate ratios of radii. It is evident that when R approaches r the value of f_w should approach infinity, whereas Ladenburg's f_w only reaches 3.4 under such conditions.

Sheppard[4] called attention to this point and derived an equation

$$T = T_\infty + C/(r-1)^2$$

in which T is the actual time and T_∞ the time required for the ball to fall in liquid of unlimited volume, C is an empirical constant which is different for each ball and r is the ratio of radii of tube and ball. His equation does not hold for values of r less than 3.

It is unfortunate that he chose to make an additive correction ("lag") instead of a ratio correction (retardation), since the choice resulted in different constants for different balls; and also apparently misled him into assigning a large correction for height of liquid, which he neglected to confirm by a variation in height of liquid or a study of bottom correction.

It is generally assumed by Ladenburg and others that the factor is a function of the ratio of

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[2] Washburn, Univ. of Illinois Bull. **21**, 21 (1924).

[3] Ladenburg, Ann. d. Physik **20**, 287; **23**, 447 (1907).

[4] Sheppard, J. Ind. Eng. Chem. **9**, 523 (1917).

radii only and not of the absolute values of the radii, or of the absolute viscosities. The former assumption was assumed also in the present investigation; but the factor was found to vary slightly with wide ranges of viscosity.

Most of the present observations were made with steel balls of seven sizes from 0.26–1.9 cm (0.104″ to 0.75″) by using glycerol in tubes of five different sizes, thus giving a large number of ratios of radii ranging up to 0.97. One series employed glucose of viscosity about 720 poises at room temperature.

As the glycerol was not absolute (though substantially anhydrous) and the difficulty of preparing and preserving absolute glycerol seemed unwarranted, the absolute viscosity was estimated by the falling ball method using a ratio within the range studied by Ladenburg. With the smaller tubes the ratio was too large for that range even with the smallest ball, but in the case of the smallest ball a value for f_w was assumed which was consistent with those found in the larger tubes with similar ratios. The factor for the other experiments was estimated from the viscosity thus found with the smallest ball. This procedure was required because the temperature of the glycerol was not precisely the same in all tubes; but in one tube it could be held constant during the several experiments. Check experiments were made in reverse order; that is using increasing size of ball and then decreasing size so that a change in temperature would show as a change in viscosity with the smallest balls. Good checks were obtained under such conditions indicating no appreciable change in temperature, nor therefore in viscosity. For this reason identical viscosities are recorded for a single series (one tube). The different viscosities in the different series are probably due to different temperatures. The results are recorded in Tables I, II and III and plotted in Fig. 1. The reciprocals of the wall factors are plotted as ordinates because the accuracy for the lower range of ratio of radii is more important. In order to satisfy the theoretical condition that f_w approaches infinity as R approaches r, functions were derived containing the factor $(r-R)$ in the denominator and using an empirical term and exponent in order to fit the observed data. The two solid curves shown are respectively the plots of the equations:

$$f_w=[r/(r-R)]^{2.25} \quad \text{or} \quad 1/(1-R/r)^{2.25} \qquad (1)$$

and

$$f_w=[(r-0.475R)/(r-R)]^4, \qquad (2)$$

of which (1) holds better for glucose of viscosity about 720 poises, and (2) holds better for glycerol of about 4 poises viscosity. The two curves are practically coincident up to a ratio of $\frac{1}{3}$ and both agree well with all of Ladenburg's observations. The upper dotted curve is the plot of Ladenburg's factor, which fails completely beyond a ratio of 0.1.

Since this paper was written, Yoshio Suge[5] has published a similar investigation covering a ratio of radii ($R/r=x$) up to 0.371. His wall factor is

$$1/(1-x)^{2.1/(1-x^2)}.$$

Within experimental error this factor is identical, for the range studied by him, with those given above. But for higher values of R/r his factor would give excessive corrections as shown in the figure by the lower dotted line. Furthermore, his factor is somewhat less convenient to use than those of the present paper.

The difference between glycerol and glucose may be due to the fact that in the former, the large balls always fall with rapid rotation about a

TABLE I. *Ladenburg's results.*

R/r	f_w	R/r	f_w
0.0107	1.0257	0.034	1.083
.01415	1.0354	.0376	1.0907
.0189	1.0447	.045	1.108
.0213	1.0525	.050	1.118
.0249	1.062	.068	1.1645
.0283	1.0664	.09	1.213

TABLE II. *Fluid glucose. Depth 18.5 cm, radius of tube 1.145 cm.*

Radius of ball (cm)	Ratio	Mean velocity (cm/sec.)	Det.	Viscosity (poises)	Wall factor
0.132	0.1153	0.0249	9	720	1.30
0.238	0.208	0.0636	4	720	1.69
0.317	0.277	0.0913	4	720	2.06
0.476	0.416	0.122	5	720	3.38
0.634	0.554	0.1074	4	720	6.62
0.794	0.694	0.0742	5	720	14.7
0.952	0.832	0.0249	4	720	61.1

[5] Yoshio Suge, Bull. Inst. Phys. and Chem. Research, Tokio **10**, 146 (1931).

TABLE III. *Fluid glycerol.*

Depth (cm)	Radius of tube (cm)	Radius of ball (cm)	Ratio	Mean velocity (cm/sec.)	Viscosity (poises)	Wall factor
45	0.422	0.132	0.313	3.15 (15 exp.)	3.20	2.33
45	0.422	0.238	0.563	3.04 2.98	3.20	7.87
45	0.422	0.317	0.750	1.30 1.34	3.20	32.7
40	0.503	0.132	0.262	3.68 (8 exp.)	3.20	1.98
40		0.238	0.474	4.73 4.86	3.20	4.91
40		0.317	0.630	3.21 3.40	3.20	12.6
40		0.476	0.947	0.097 0.092	3.20	985
136	0.990	0.132	0.1333	3.89 3.89 3.89	4.65	1.35
136	0.990	0.238	0.240	9.09 8.96	4.65	1.88
136	0.990	0.317	0.320	12.14 12.04	4.65	2.50
136	0.990	0.476	0.481	13.13 13.13	4.65	5.18
136	0.990	0.634	0.640	8.23 8.28	4.65	14.5
136	0.990	0.794	0.802	2.60 2.58	4.65	72.5
136	0.990	0.952	0.962	0.0935	4.65	2870
136	0.990	0.132	0.1333	3.07 3.09	5.88	1.35
		0.238	0.240	7.22	5.88	1.88
		0.317	0.320	9.92	5.88	2.42
		0.476	0.481	10.48	5.88	5.14
		0.634	0.640	6.85	5.88	13.9
		0.794	0.802	2.32	5.88	63.8
		0.952	0.962	0.0688	5.88	3070
136	1.226	0.132	0.1077	4.19 (5 exp.)	4.57	1.274
		0.238	0.1941	10.65 10.82	4.57	1.611
		0.317	0.2586	15.49 15.66	4.57	1.97
		0.476	0.388	21.0 21.7	4.57	3.23
		0.634	0.517	19.4 20.0	4.57	6.17
		0.794	0.647	13.0 13.13	4.57	14.55
		0.952	0.776	5.35 5.42	4.57	50.5
36	2.35	0.132	0.0561	5.20 (7 exp.)	4.10	1.135
36	2.35	2.270	0.970	0.248	4.10	5700

horizontal axis, and so perhaps disturb the true viscous relations. Instead of falling down the axis of the tube, they always fall near one side of the tube. The side of the ball closest to the tube wall falls very rapidly, while the side farthest from the wall is carried upwards by the rising stream of liquid passing the ball.

On the other hand it may be that glucose is not truly viscous, but partly plastic, thus accounting for the difference.

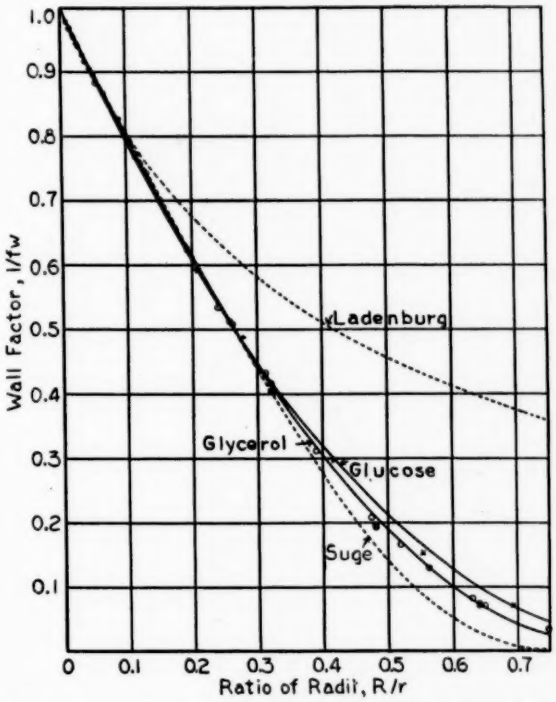

FIG. 1. Reciprocal of the wall factor as a function of the ratio of ball diameter to tube diameter. Black dots, Ladenburg; crosses, glucose; circles, glycerol.

The maximum rate of fall for a ball of given material and definite size tube results when the ratio R/r is 0.47 with Eq. (1) or 0.43 with Eq. (2). This is of importance if we are studying a very viscous material and wish accurate results within a reasonable time. However, the rate is only about 15 percent less when R/r is $\frac{1}{3}$; and this ratio is recommended as insuring greater accuracy of wall factor, and in the case of glass less error due to corrosion of the walls.

Because of the large wall factor, it was suggested that the influence of the bottom might be considerable. This would appear as a decrease of rate as the ball approaches the bottom. This effect was studied by means of a weighted celluloid ball of radius 0.461 cm and density 1.26 (only a trifle higher than that of glycerol so as to get a slow rate) falling in glycerol in a narrow burette (radius 0.503 cm) which was chosen so as to have a tube with very uniform bore and accurate uniform marks to read position. A flat false bottom was provided by jamming in a cork stopper with its top (big end) at the 3.0 ml mark.

The time was read at every 0.1 ml mark with a stop watch, and a second stop watch used to time the last 0.1 ml independently. From 0.3 ml to 3.0 ml the average time was 17.38 sec. per 0.1 ml and the individual times never varied more than 1 sec. from this mean. The time for the last 0.1 ml was 17.6 sec., indicating not more than about 1 percent retardation at a distance of 1 mm from the bottom. Several other experiments which use larger and smaller balls and tubes likewise failed to detect an appreciable bottom correction. I conclude therefore that it is negligible.

A correction for the surface of liquid must be equally negligible assuming, of course, that the ball is completely immersed before an initial observation on rate of fall. The ratios of radius of ball to height of liquid studied by Ladenburg (maximum 0.008) were so small that it is doubtful if his precision of measurement was sufficient to justify the correction which he proposed for limited height of liquid; especially in view of the complete absence of any effect under the greatly exaggerated conditions in the present investigations. It seems preferable to omit this correction entirely.

Erratum:

Interpretation of the Resistivity Prospecting Method for Horizontal Structures

(PHYSICS **4**, 307, 1933)

IN the paper of the above title which appeared in the September issue, Fig. 3 was repeated for Fig. 4. The correct Fig. 4 is given here.

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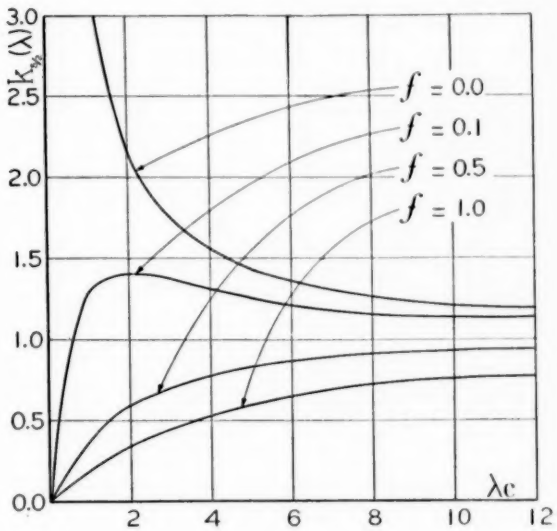

FIG. 4. The kernel, $k_{s/2}\lambda$.